Using Laser Ablation Inductively Coupled Plasma Mass Spectroscopy (LA-ICP-MS) to Determine the Provenance of the Cobalt pigment of Qinghua Porcelain from Jingdezhen in Yuan Dynasty of China (1271-1368AD)

Zhu Tiequan¹ Ding Xing² Chapurukha M. Kusimba³ Feng Zeyang¹

1 School of Sociology and Anthropology of Sun Yat-sen University, Guangzhou, China, 510275;

2 State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China;

3 Department of Anthropology, American University, Washington, DC 20016, USA.

Corresponding author: Zhu Tiequan, College of Sociology and Anthropology of Sun-Yat sen University, 135, Xigangxi Rd, Guangzhou, 510275, China

Email: zhutq@mail.sysu.edu.cn

Corresponding author: Ding xing, State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China;

Email: xding@gig.ac.cn

Abstract

The provenance of cobalt mineral of the blue decoration in Yuan Qinghua porcelain would reveal the technological and cultural interaction between ancient China and the Islamic world. However, the limitation of conventional methods in the determining trace elements of the blue decoration hampered the deep research on provenance of the cobalt mineral. In the paper, we employed the good advantage of Laser-ablation-inductively-coupled-plasma-mass-spectroscopy (LA-ICP-MS) to determine the major element and trace elements of blue decoration of the different type of Qinghua successfully. The blue decoration of all different types of samples shared the same characteristics of higher FeO and lower Mn, which suggested the potter adopted the non- native cobalt material of China to paint the Yuan Qinghua in Jingdezheng, and the difference on the outside appearance of blue decoration of different samples were supposed to be related to the tenor of ore, the different treatment process of cobalt material and the firing process in the kiln. In addition, the significant differences on the element concentrations of Cu, Ni, Pb, Zr

and Sb in the blue decoration between Yuan Qinghua and the Islamic blue and white wares of 13-14th century provided a new evidence to discuss the provenance of the cobalt of Yuan Qinghua porcelain.

Key words: Yuan Qinghua porcelain ,the Blue decoration ,Cobalt mineral , LA-ICP-MS

1. Introduction

As one of the most widely distributed Chinese porcelains in the world, Qinghua porcelain with the skillful manufacturing technology and artistic merits, was sought after by the ruler, connoisseurs, and commoners in different counties for hundreds of years. The successful invention of Qinghua is presently credited to Gong Xian potters of Henan Province during the Tang Dynasty (618-907AD)^[1-2]. However it was during Yuan Dynasty (1271-1368AD)that the technology of making Qinghua porcelain matured and achieved its global prominence, and the kilns of Jingdezhen, Jiangxi Province, are widely believed to have pioneered the development of Qinghua porcelain that time^[3]. Since the Yuan Dynasty, large volumes of Qinghua porcelains were exported to different regions of the world including Central Asia, West Asia, Southeast Asia and East Africa. When it came to the the 17th century, direct trade between China and Europe increased, and the arrival of blue and white porcelain had become to play a key role in the development of Portuguese and Dutch fine faience^[4].

The provenance of cobalt mineral in Yuan Qinghua porcelain has long been of interest to scholars worldwide. Cobalt pigments in Yuan Qinghua porcelain have been divided into three groups: 1) a gaudy blue type with apparent spot of iron oxides was supposed to adopt the imported cobalt mineral, 2) a blue-gray color was thought to be native cobalt of China, and 3) a gray blue color with slight blue was mixture of the exported and the domestically produced^[5]. The China native cobalt pigment mainly referred to the material produced in the Yunnan, Jiangxi, and Zhejiang. The provenance of the imported material was thought to be either ancient Persia^[6],or Gansu, Xinjiang in the northwest of China or some area in the central Asia^[7].

The application of geochemistry trace element analysis has played and continues to play a critical role in resolving provenance and sourcing of archaeological artifacts that is absolutely

necessary for addressing other questions including technology, trade, distribution, and organization, consumption and so on^[8]. Since 1950s', lots of analytic instruments including EMPA, μ -XRF, SRXRF, PIXE, etc^[9,10,11,12], were employed to analyze the blue decoration of Yuan Qinghua in an effort to discern the provenance of its cobalt mineral, however, these early efforts were hampered by the inability of these techniques to detect a complete range of trace elements. Consequently, the sources of blue decoration of the blue white porcelain have remained poorly understood. Although other analytic methods, including ICP-AES, NAA and ICP-MS, have the capability to detect the trace elements, their wide application has often been hampered by the fact that they are destructive and thus now particularly unsuitable for analysis of the blue decoration between the glaze and body of wares.

The capability of Laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS), to detect trace elements and isotopes, provides this analytic technique with the advantage of *in situ* micro-analysis, high precision, selectivity, sensitivity, and lower detection limits, making it one of the most widely used tools to research geological material^[13-14]. We carried out LA-ICP-MS analysis on the blue decoration and glaze of 20 pieces Yuan Qinghua porcelain samples from Jingdezhen and 3 samples of the Islamic blue and white glazed pottery of 13-14th century excavated from Mtwapa in Kenya. This paper reports the results of our study and discusses its implications for understanding the provenance of the cobalt material in the blue decoration of Yuan Qinghua.

2. Experimental

2.1. Sample description

In our work, 20 pieces of Yuan Qinghua shards recovered at *Luomaqiao and Shibaliqiao* archaeological site in Jingdezhen of Jiangxi province, China, were provided by the College of Jingdezhen Ceramics. Seven samples with the characteristic of the exported blue cobalt material were respectively labeled as YJ1, YJ2, YJ3, YJ4, YJ5, YJ6 and YJ7, and five samples with the characteristics of typical Chinese native material were labeled as YG1, YG2, YG3, YG4 and YG5, and eight samples with the characteristic of the admixture material and were labeled as YH1, YH2,

YH3, YH4, YH5, YH6, YH7 and YH8. Photograph of the typical samples were shown in Fig.1. In addition, three samples of Islamic blue and white ware shards of 13-14th century excavated at Mtwapa Kenya, were labeled as SWA1, SWA2 and SWA3, which are identified to be imported from Ancient Persia.

2.2. Analytic methods

A small piece of Yuan Qinghua sample with blue decoration was cut from the shards, and mounted on the stubs with double-sided adhesive tape and then buried by a 4:1 mixture of the epoxy resin and hardener within a plastic pipe in diameter of 2.5cm for making a target. After naturally consolidated for 24 hours, it was polished carefully to remove the resin covered on the samples and thus to expose a cross-section of blue decoration for every sample. Finally the sample in the target was numbered with the Arabic numeral corresponding to its original labeled number for testing, as shown in the Fig2.a.

The analysis was carried out at the State key Laboratory of Isotope Geochemistry in the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The Analytic instrument was Agilent 7500a ICP-MS coupled with a Resonetics Resolution M-50 laser-ablation (Resonetics, UAS), with a two-volume sample cell designed to avoid cross the contamination and reduce background flushing time, and a Squid smoothing device producing less statistical error induced by laser ablation pulse and a compute-controlled high precision X-Y Stage. The ablated aerosol of samples was carried to ICP source with He gas, where the matter was dissociated, atomized and ionized. The ions were then injected into the vacuum chamber of a quadrupole system, which discriminated the ions depending upon their mass-to-charge ratio. The detection limits of the ICP-MS for trace elements are mostly 10ppb with uncertainties of 5-10%^[13]. In this analysis, laser ablation was operated at a constant energy of 80mJ and repetition rate of 10 Hz, with a spot of 69 μ m. Each analysis incorporated a background acquisition of approximately 25-30s (gas blank). Each analytic batch consisted of two ablations on the NIST610 standard at the beginning and the end and on the NIST612 in between every-four samples. NIST610 was used as the external calibration standard, ²⁹Si as an internal standard to correct possible instrumental drift or changes in the ablation efficiency, whose concentration was determined by Micro X-ray spectroscopy (μ -XRF), while NIST612 as a monitoring standard to evaluate the precision and accuracy of

measurements. The samples adapted the average concentration obtained by 3 ablations dispersedly distributed in one sample. Off-line analysis and integration of background and analyzed signals and time-drift correction and quantitative calibration were performed by ICPMSDateCal.^[15] The detection limit of most trace element is to several ppb, except for some elements including Cr, Ni, Cu and Zn, with detection limit of several ppm. The reproducibility of the elements was <5%, while the accuracy was mostly < 10% (Table.1). The photograph of the analyzed area of samples and its representative signal spectrum was shown in Fig 2.b and Fig.3.

3. Discussion

3.1. Major element

Eight major elements including Mg, Al, Si, P, Ca, Ti, Fe, Mn and Co on the blue decoration of the samples were detected. Usually the main colorant elements of the blue decoration was cobalt, However the existence of the iron and manganese may affect the outside color^[15]. As the samples contained few MnO in the range of 0.09-0.16%, here only element Co and FeO were considered. In order to better reflect the difference on the Co and FeO of different samples, the ratio of Co/FeO was calculated. As illustrated in Fig.4, it is easy to find that the YJ had higher ratio Co/ FeO, compared with YH and YG samples. As is known, the more pure of cobalt pigment, the bluer that blue decoration will appear. Hence the chemical difference on the ratio Co/FeO could explain why the YJ samples appeared blue and gaudy, while some exceptional YH and YG samples which contained higher ratio of Co/FeO and still appeared gray, it probably related to the firing process including temperature, atmosphere, duration of high temperature.

It also must be mentioned that the blue decoration of all the samples exhibited the apparent characteristics of lower Mn, which was totally different from that of Yuan Qinghua produced in the Yunnan province, the southwestern of China^[12]. As both historical literature and geological investigation have revealed that the asbolite, bearing high content of Mn (16.84-47.96%), was widely distributed in the southern China including Yunnan, Jiangxi, and Zhejiang^[16-17], it could indicate the potter did not use the native cobalt material paint the Yuan Qinghua of Jingdezhen, but adopted a similar non-native cobalt mineral of China, and the outside difference appeared on the blue decoration of different samples were supposed to be related to the tenor of cobalt ore and

the different treatment process of cobalt material and the different firing process in the kiln.

3.2. Trace element

The trace elements of the blue decoration doesn't just relates to the pigment, but to the mixture of pigment and glaze. To acquire the trace characteristics of the pigments, we compared the data of trace elements of both blue decoration and the pure glaze (Table.3), and found that only the elements As and Sb were relatively higher than that of the corresponding glaze except for one or two samples, as shown in Fig.5.

The chemical researches showed arsenic with the boiling point of 847℃ would evaporate in the higher temperature of 1250℃, which was redeemed the firing temperature of Qinghua^[15]. Even though, there were still a certain amount of As reserved in the blue decoration of samples, which indicated the mineral of the blue pigment of Yuan Qinghua was a kind of cobalt mineral in high content of arsenic, which further confirmed the previous research^[7]. In the meantime, the geological investigation revealed that Sb was very similar with As in chemical properties would usually be enriched in the mineral with High content of As^[18,19], that could explain why the Sb could be detected in the blue decoration.

There were no clear-cut elemental difference on the As, Sb and other trace elements among three types of Yuan Qinghua samples, which further ascertained that all samples adopted the similar cobalt mineral as the original material.

3.3. Difference on the blue decoration between the Qinghua and Islamic blue and white wares

Since it was a great pity that we could not collect ancient Persian cobalt material which was redeemed to paint the Yuan Qinghua for the direct comparison, Here in this work, we compared the data of blue decoration of Yuan Qinghua and that of the 13-14th centenary Islamic blue and white wares, and attempted to provide some basis for the discussion of the provenance of cobalt material of Yuan Qinghua.

Seen from the Table.2, the Islamic blue and white samples also contained less content of MnO in the range of (0.05-0.18%), and the characteristic of lower Mn was very similar with that of the Yuan Qinghua, which was just in accordance with the previous studies^[6]. In the meanwhile ,

Different from other Islamic blue and white wares with higher Zn in the blue decoration reported by other scholars^[20,21], Zn in the Islamic blue and white samples was much lower, in the range of 50.69~119.75μg/g, which just was in accordance with that the blue and white ware of 13-14th century from ancient Persia^[22] and it was also similar with that of Qinghua samples (Zn: 48.79~145.18μg/g).

In the meanwhile, there were distinctive differences between the blue decoration of Yuan Qinghua porcelain and that of Islamic wares on the concentration of other elements including the Sc, V, Cr, Ni, Cu, As, Sr, Ba, Pb, Th, Ga, Rb, Nb, Sn, Cs, Ta, etc. However, only Ni, Pb, Cu, Zr and Sb beard the chemical characteristic of the original blue pigment, after a careful comparison of the blue decoration of the Islamic blue and white wares and that of its glaze (Table.2 and Table.3). As shown Fig.6, the Islamic samples had higher Ni(208.45~353.95μg/g), Cu(702.75~3443.07μg/g), Zr(83.96~194.36μg/g), Pb (82.86~90.91μg/g) and lower (0.38~0.93μg/g), while the Qinghua samples had lower Ni(4.80~94.63μg/g), Cu (16.67~127.69μg/g), Pb(10.49~37.37μg/g), Zr(16.15~57.82μg/g) and higher Sb(0.81-18.38μg/g). Due to the detection limit of the X ray spectroscopy, trace elements including Ni, Pb, Zr and Sb of the 13-14th Persian ceramic have not been detected in the previous studies^[22], however which could be used to discuss the difference on the blue decoration of Yuan Qinghua and that of the Islamic white and blue wares.

The above difference may suggest Yuan Qinghua porcelain didn't use the similar cobalt material of the Islamic blue and white wares analyzed here, but other cobalt mineral in ancient Persia or other places. However, some scholars have assumed that these difference were caused by differences in kiln temperatures and treatment processes of the cobalt material for two kinds of ceramic. As it is easy to understand the high temperatures of 1250° for firing ancient Qinghua kilns in Jingdezhen would have easily vaporized the volatile elements including As, Zn, Sb etc, and the fine and the complex treatment process of cobalt material, including floating selecting and firing, would also have resulted in the removal of a certain amount of the copper and other elements^[20]. So whether the above assumption is right or not, the simulation experiment is necessary to conclusively be carried out, and in the meanwhile, much more samples need being analyzed systematically to determine the precise locale from where cobalt blue originated.

4 Conclusion

This study has revealed that the blue decoration of all different samples shared the same characteristics of higher FeO and lower Mn, and YJ samples had higher ratio of Co/FeO, which suggested potters did not use native cobalt material to paint the Yuan Qinghua in Jingdezhen but adopted a similar non-native cobalt mineral of China, and the difference in the external appearance of blue decoration in the different samples probably related to the tenor of ore, the differential treatment of cobalt material, and the firing processes in the kiln. In addition, the study also found there were some differences in the concentration of elements including Cu, Ni, Pb, Zr and Sb in the blue decoration of Yuan Qinghua and that of the Islamic blue and white wares, and further research is necessary to conclusively determine whether these differences is caused by differential kiln firing temperatures and treatment processes of cobalt mineral.

Considering that only a very limited number of samples were examined here, this research is preliminary, but it shows the promise and clear advantages of LA-ICP-MS in determining the blue decoration of Qinghua and the related samples, Our ongoing collaborative work aims to analyze more samples drawn from archaeological excavations and carefully museum collections to expand our work and eventually confirm with precisely the provenance of cobalt mineral of Yuan Qinghua porcelain.

Acknowledgment

The paper was supported by the National Science Foundation of China(No: 41103013) and the US National Science Foundation (SBR 9024683, BCS 9615291, BCS 0648762 , BCS-1030081)

Reference

- [1] X. J Feng, Origin and development of the Qinghua porcelain, Journal of History Museum, 1994(2), 29-39.(In Chinese)

-
- [2] X Sun, L Liu, Z Zhao, M Guo, M Bao, J Zhao, J Tian, J Zhang, L Shen, Y Zhou, L Li and M Guo, Excavation of Huangye Kiln Site in Gong county of Henan province, Huaxia Archaeology, 2007 (4), 106–129. (In Chinese)
- [3] X.M Feng, China ancient ceramic, Shanghai: Shanghai Chinese Classsic Publishing House, 2004, pp.452
- [4] C. J. A Jorg, Interaction in the ceramics oriental porcelain and Delfware, Hongkong: Press of Hongkong musuem of art, 1984, pp. 60-64.
- [5] F.K Zhang, Science of Chinese ancient ceramic, Shanghai:Shanghai Art Press, 2000, pp.119. (In Chinese)
- [6] H. Garner, The Use of Imported and Native Cobalt in Chinese Blue and White, Ars Oriental, 1956(2), 43. (In Chinese)
- [7] Y.C Chen, Y.Y Guo and Z.Z Zhang, An investigation on Chinese blue and white porcelain and it blue pigment, Journal of the Chinese Ceramic Society,1986(2), 164–168. (In Chinese)
- [8] C.S Wang, Y. Qin and Q. P. Qiu, Chief history of research the provenance of the artifact (ed: C.S Wang), Archaeomtry Review □, Hefei: University of Science and Technology of China, 2003, pp.26-32. (in Chinese)
- [9] Y.Y Guo and W. J Qian , An investigation of some Yuan Dynasty blue and white porcelain shards - about new discovery of cobalt color pigment of Yuan blue and white wares //In proceedings of the international symposium on ancient ceramics, Shanghai :Shanghai Science and Technology literature press, 2005, pp.157-166. (In Chinese)
- [10] H.S Cheng and Z.Q Zhang, The identification of chenghua white and blue porcelain by using PIXE and multivariate statistical analysisJournal of Fudan University (Science Version), 2001(1),96-98. (In Chinese)
- [11] J Wu, J.Z Li, Z.Q Deng and C.S Wang, Study on dating of Qinghua porcelain of different dynasties Science in China, Series E, Engineering and Materials Science, 34, 2004(5), 516–24.
- [12] R Wen, C.S Wang, Z.W Mao, Y.Y Huang and A.M Pollard , the Chemical Composition of Blue Pigment on Chinese Blue and white Porcelain of The Yuan and Ming Dynasties (AD 1271–1644), Archaeometry, 49, 2007(1), 101–115.

-
- [13] X.L Tu, H Zhang, W.F Deng, M.X Ling, H.Y Liang, Y Liu and W.D Sun, Application of RESOLution in-situ laser ablation ICP-MS in trace element analyses, *Geochimica*, 40, 2010(1), 81-89. (In Chinese)
- [14] X Ding, Y.H Hu, H. Zhang, C.Y Li, M.X Ling and W.D Sun, Major Nb/Ta Fractionation Recorded in garnet amphibolite facies metagabbro, *The Journal of Geology*, 121, 2013, 255-274.
- [15] Y.S Liu, Z.C Hu, S. Gao, D Günther, J Xu, C.G Gao and H.H Chen, In situ analysis of major and trace elements of anhydrous minerals by LA-ICP-MSLA-ICP-MS without applying an internal standard, *Chemical Geology* 257, 2008, 34-46.
- [16] Y.C Chen and Y.Y Guo, Discussion on the Provenance of Cobalt Pigment of Yuan Qinghua Porcelain , *China Ceramic*, 1993 (5), 57-62.(In Chinese)
- [17] J.Z Li, History of Chinese science and technology. volume of ceramic, Beijing :Science Press of China, 1998, pp.325-359. (In Chinese)
- [18] G. Luo, Crystallographic and optical mineralogy, Beijing :Press of Geology, 2009, p.147. (In Chinese)
- [19] The edition team of Gui Yang Insitute of Geochemistry of CAS, the Identical handbook of mineral power crystal by X-ray diffraction, Beijing :Science Press of China, 1978, pp.42-56. (In Chinese)
- [20] R. Wen and A.M Pollard, Comparative study of cobalt blue pigment on Chinese blue and white porcelain and Islamic glazed pottery ,Thirteen -Seventeenth Centuries, (eds: B Mccarthy, E.S Chase, L.A Cort, J.G Douglas and P Jett), *Scientific Research on Historic Asian Ceramics*. London: Archetype Publications Ltd, 2009, pp.24-32;
- [21] N. Wood, M.S Tite, C. Doherty and B. Gilmore, A technological extermination of nine-tenth century AD abbasid blue and white ware from Iraq, and its comparison with eighth century AD Chinese blue and white sancai ware, *Archaeometry* 49, 2007 (4), 665–684.
- [22] M. Cowell, and F. Zhang, in Catalogue of Late Yuan and Ming ceramics in the British Museum (ed. J. Harrison-Hall), catalog of Late Yuan and Ming ceramics in the British Museum ,British Museum Press, London, 2001, pp.601–605.

Table.1

Table.1. The reference values and analyzed values of international reference material used for calculation in this study (ug/g)

		MnO	FeO	Co	Ni	Cu	Zn	As	Rb	Sr	Zr	Nb	Sn	Sb	Cs	Ta	Pb	Th
SRM 612	MV 1	53.11	60.11	33.99	40.96	35.89	40.20	31.99	31.31	78.31	36.09	34.79	34.71	32.16	40.67	37.20	38.87	37.09
	MV 2	53.39	60.11	34.07	39.66	37.28	41.91	32.69	30.74	77.26	36.65	34.83	35.36	32.38	40.93	36.79	38.89	36.46
	MV 3	52.59	60.11	33.89	38.46	36.05	40.64	33.46	30.84	76.65	35.87	34.55	34.83	31.80	40.40	37.01	37.57	36.93
	Average	53.03	60.11	33.98	39.69	36.41	40.92	32.71	30.96	77.41	36.21	34.72	34.97	32.11	40.67	37.00	38.44	36.83
	RV	0.00	0.01	35.00	38.80	37.00	38.00	37.00	31.40	78.40	38.00	40.00	38.00	38.00	42.00	40.00	38.00	37.79
	STD	0.33	0.00	0.08	1.02	0.62	0.72	0.60	0.25	0.69	0.33	0.12	0.28	0.24	0.22	0.17	0.62	0.27
	RSD	0.00	0.00	0.22	2.57	1.70	1.77	1.83	0.81	0.89	0.91	0.35	0.80	0.75	0.53	0.45	1.62	0.73
SRM 610	MV 1	613.73	551.55	394.40	431.02	425.74	441.96	318.13	415.53	511.79	425.17	425.92	390.35	373.77	360.73	446.80	414.61	449.16
	MV 2	613.73	551.55	401.19	457.22	429.82	449.20	324.66	426.81	518.20	440.92	429.58	398.98	378.60	365.84	457.68	426.68	458.86
	MV 3	613.73	551.55	410.20	456.00	433.44	456.76	323.40	421.54	509.23	439.53	420.57	398.34	378.21	354.36	449.08	418.44	452.34

	Average	613.73	551.55	401.93	448.08	429.67	449.31	322.06	421.29	513.07	435.21	425.36	395.89	376.86	360.31	451.19	419.91	453.45
	RV	0.06	0.06	405.00	458.70	430.00	456.00	317.00	425.70	515.50	440.00	419.00	396.00	369.00	361.00	452.00	426.00	457.20
	STD	0.00	0.00	6.47	12.07	3.15	6.04	2.83	4.61	3.77	7.12	3.70	3.93	2.19	4.70	4.69	5.04	4.04
	RSD	0.00	0.00	1.61	2.69	0.73	1.34	0.88	1.09	0.74	1.64	0.87	0.99	0.58	1.30	1.04	1.20	0.89

MV = Measure Value , RV = Reference Value

* The reference values of trace elements in NIST612 and NIST610 from the GeoReM database (2011,<http://georem.mpch-mainz.gwdg.de/>)

Table.2

Table 2 The Analytic Result of the blue decoration of Samples by LA-ICP-MS (elements of Mn,Fe,Co : wt%, other elements: µg/g)

	MnO	FeO	Co	Sc	V	Cr	Ni	Cu	Zn	As	Rb	Sr	Zr	Nb	Sn	Sb	Cs	Ta	Pb	Th
YJ-1	0.10	1.83	0.78	0.90	14.21	2.18	11.37	61.49	108.98	76.04	274.37	119.87	22.32	12.09	10.88	5.84	12.20	3.72	37.28	1.75
YJ-2	0.11	2.30	0.49	1.01	3.86	3.74	25.66	31.66	83.69	40.07	305.53	117.22	19.78	11.44	7.60	5.14	23.59	3.30	14.77	2.16
YJ-3	0.10	5.84	0.94	1.05	5.56	5.42	45.04	47.16	67.36	564.88	290.98	141.05	25.80	12.31	4.10	1.34	24.51	3.84	11.70	2.46
YJ-4	0.09	3.72	0.84	0.88	4.01	1.24	32.43	36.18	105.68	50.91	371.64	120.76	24.11	13.22	17.64	2.85	17.37	4.21	17.42	1.86
YJ-5	0.15	4.69	2.91	0.79	4.64	3.42	84.15	24.41	145.18	281.58	287.96	139.36	26.33	11.95	5.02	18.05	13.73	3.57	30.40	2.49
YJ-6	0.16	2.92	1.00	1.14	4.33	2.97	60.19	35.93	121.76	63.79	371.78	122.37	27.43	18.27	5.20	3.36	23.30	5.05	37.37	2.81
YJ-6	0.10	2.56	0.72	1.14	4.45	3.20	9.74	23.74	49.32	22.05	396.35	88.18	16.61	12.97	4.78	3.49	22.51	3.66	11.68	1.71
YH-1	0.15	10.12	2.15	1.23	5.84	5.31	59.43	127.69	123.61	262.27	297.67	149.86	27.15	16.35	10.16	18.38	15.74	4.80	21.34	2.36
YH-2	0.09	4.83	0.62	0.94	4.73	6.15	6.41	18.59	106.00	38.76	374.47	137.00	24.87	13.92	32.45	1.38	29.17	4.85	23.09	2.43
YH-3	0.08	1.47	0.29	0.64	2.83	3.08	17.75	70.43	85.40	14.36	254.66	141.58	16.15	14.37	4.22	1.53	14.31	3.87	26.80	2.04
YH-4	0.12	3.60	0.35	1.20	5.97	2.80	27.70	16.67	96.49	7.60	280.14	162.39	26.59	15.72	8.39	1.83	19.10	4.86	13.85	2.61
YH-5	0.13	1.42	0.14	0.64	3.31	4.07	8.47	22.09	70.46	5.79	249.14	114.68	57.82	10.10	3.73	0.81	13.82	2.96	13.97	2.12
YH-6	0.13	3.74	1.06	0.87	4.54	7.35	33.68	21.75	140.77	109.60	344.75	102.68	24.77	17.07	16.73	7.63	25.72	5.69	26.50	2.26

YH-7	0.08	1.35	0.08	0.86	4.51	9.59	92.33	28.89	48.79	3.42	332.04	130.42	18.80	13.22	10.06	2.97	22.83	3.72	10.49	1.74
YH-8	0.13	7.80	0.79	1.24	10.32	2.07	14.32	35.34	91.03	17.00	369.02	148.65	29.18	14.73	16.89	3.86	22.39	3.74	33.69	4.37
YG-1	0.14	4.01	0.89	1.29	8.83	9.48	94.63	31.42	77.08	87.81	331.35	125.95	26.92	20.90	8.89	3.88	23.63	5.99	17.28	2.80
YG-2	0.12	3.11	0.26	1.36	4.63	2.89	7.56	27.73	121.97	75.19	396.69	150.54	28.88	15.42	18.51	2.57	26.03	4.47	34.99	3.11
YG-3	0.10	1.76	0.19	1.15	6.35	2.25	5.32	22.79	101.94	197.97	240.44	171.70	19.27	13.32	5.15	1.79	13.21	3.80	33.46	2.22
YG-4	0.12	5.19	0.87	1.12	4.66	1.91	4.80	32.62	61.66	13.12	521.45	113.71	18.78	12.39	20.05	1.33	29.80	3.38	20.05	2.95
YG-5	0.13	1.72	0.28	0.85	5.86	3.12	9.35	33.43	128.01	16.65	223.31	183.15	30.61	14.75	6.52	3.05	8.86	4.52	26.58	1.79
SWA-1	0.18	2.02	0.03	6.61	120.87	49.93	208.45	3443.07	50.60	15.41	31.45	340.94	194.36	9.05	3.25	0.38	0.56	0.81	90.91	11.47
SWA-2	0.09	2.23	0.83	4.20	32.80	40.26	353.95	702.75	113.38	4840.80	151.82	328.59	83.96	5.51	2.49	0.93	6.11	0.46	82.95	5.30
SWA-3	0.14	2.07	0.48	4.04	32.52	32.54	273.02	1974.14	119.75	4285.94	201.40	354.68	85.43	7.96	3.74	0.84	8.10	0.53	82.86	18.18

Table.3

Table. 3. The Analytic Result of the glaze of Samples by LA-ICP-MS (elements of Mn,Fe : wt%, other elements: µg/g)

	MnO	FeO	Co	Sc	V	Cr	Ni	Cu	Zn	As	Rb	Sr	Zr	Nb	Sn	Sb	Cs	Ta	Pb	Th
YJ-1	0.10	0.57	39.25	0.65	10.51	4.11	13.62	47.92	103.63	12.64	264.11	165.80	21.40	11.98	9.64	3.65	10.15	3.85	35.15	1.75
YJ-2	0.08	0.51	20.52	13.21	14.18	16.48	44.05	38.08	65.44	18.85	206.85	131.79	27.84	23.08	15.92	12.20	25.00	15.68	21.39	13.75
YJ-3	0.11	0.74	50.39	0.85	2.74	7.11	11.08	33.77	69.96	3.86	288.72	163.43	33.30	19.73	3.94	0.66	21.66	6.00	14.75	2.16
YJ-4	0.11	0.87	138.49	0.78	4.30	1.24	15.74	43.88	115.66	26.17	257.10	194.65	21.38	13.63	14.29	2.77	9.83	3.90	16.15	1.97
YJ-5	0.13	0.71	12.71	0.88	3.52	3.01	21.33	30.05	120.06	4.70	280.17	163.73	26.67	14.34	4.66	2.06	12.40	4.54	29.10	1.88
YJ-6	0.12	0.74	2.34	0.93	2.33	1.04	21.42	31.65	90.07	12.72	301.93	128.65	42.60	15.01	4.66	2.33	14.22	4.56	22.82	2.20
YJ-6	0.10	0.66	28.50	0.70	1.14	3.60	23.02	35.45	61.02	2.06	391.65	141.57	13.62	12.37	7.90	3.45	23.11	4.04	16.13	1.46
YH-1	0.13	0.90	7.97	0.70	2.81	3.34	21.25	32.50	65.49	8.65	251.94	180.17	25.15	15.34	4.16	1.12	12.37	4.29	10.88	1.78
YH-2	0.09	0.78	3.65	1.02	4.16	5.60	3.64	21.81	83.17	7.15	345.56	195.78	19.44	18.13	23.17	1.06	19.37	7.64	10.63	1.85
YH-3	0.10	0.47	6.20	0.64	2.87	0.27	17.65	84.27	94.72	4.83	281.53	180.67	22.44	14.88	4.27	1.38	15.85	4.30	26.52	1.92
YH-4	0.12	0.89	13.17	1.06	4.63	5.52	26.20	26.49	91.61	27.89	247.47	199.58	27.42	12.78	4.98	1.47	12.08	4.02	9.80	1.96
YH-5	0.11	0.91	18.56	0.97	3.76	5.50	9.39	17.07	118.02	6.71	337.44	129.16	26.22	21.25	17.72	3.27	29.95	5.44	32.34	2.87
YH-6	0.13	0.71	6.14	0.75	3.63	10.39	11.89	30.03	80.66	7.49	273.02	168.71	17.91	17.31	4.09	0.71	15.37	5.81	11.66	1.60

YH-7	0.12	0.69	15.65	0.70	4.23	3.67	7.06	24.50	89.70	11.23	324.16	142.65	30.51	23.77	7.42	2.46	14.80	6.38	21.56	5.24
YH-8	0.09	0.65	3.18	0.91	3.15	0.18	22.41	26.78	70.95	7.00	284.94	173.05	18.28	12.94	9.37	2.81	19.71	3.93	14.60	1.96
YG-1	0.10	0.71	4.44	0.84	4.74	5.62	5.36	21.79	82.92	48.82	263.38	173.56	22.37	14.07	4.69	1.62	15.36	4.61	33.30	2.07
YG-2	0.11	2.09	456.91	1.60	4.42	3.28	5.31	26.59	127.57	29.58	417.26	138.92	42.41	15.10	19.08	2.32	30.03	3.94	36.12	3.20
YG-3	0.09	0.50	3.14	0.69	8.63	4.72	6.23	31.79	106.52	9.36	192.96	213.02	23.97	15.46	4.96	3.00	7.62	4.41	17.52	1.86
YG-4	0.08	0.65	10.56	0.83	2.09	2.14	2.30	26.50	57.24	12.28	361.34	154.19	27.47	12.34	13.18	0.94	17.26	3.37	11.37	1.77
YG-5	0.12	0.48	3.44	1.31	6.03	4.43	4.79	47.94	74.50	8.84	363.66	107.61	16.99	12.07	2.70	2.47	23.06	3.45	21.52	1.73
SWA-1	0.16	1.96	7.33	5.33	122.60	41.40	16.05	531.55	46.73	25.44	28.10	252.89	156.50	8.00	2.57	0.33	0.50	0.73	41.47	9.64
SWA-2	0.06	1.24	16.04	3.16	22.69	25.33	12.61	471.12	88.07	92.28	133.19	413.61	69.16	4.96	1.27	0.41	5.23	0.47	39.55	5.78
SWA-3	0.07	1.19	13.93	3.59	26.10	25.03	14.82	1036.62	76.51	22.88	180.97	464.36	72.58	5.21	1.19	0.11	7.63	0.45	37.01	6.98

Fig.1

YJ-3 1 cm

YH-8 1 cm

YG-1 1 cm

YG-3 1 cm

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6

Fig.1 Photo of the typical Yuan Qinghua porcelain

Fig.2 Photographs of Yuan Qinghua samples for LA-ICP-MS analysis (A: the prepared samples, B: the blue decoration tested)

Fig.3 LA-ICP-MS Signal Spectrum on the blue decoration of Yuan Qinghua sample

Fig.4 the Ratio of Co/FeO in Blue Decoration of Yuan Qinghua

Fig.5 The comparative diagram of concentration of trace elements in blue decoration and that of the corresponding glaze of samples

Fig. 6 The plot-box diagram of trace elements in the blue decoration of different samples